Low-Temperature Cathode-Supported Electrolytes

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Objectives

- Perform studies on nanocrystalline electrolyte thin films.
- Prepare graded porous structures for use as substrates for electrolytes thin films.
- Perform electrical characterization and testing of planar single cells.

Key Milestones

- Characterized films of 16% Sc:ZrO_2.
  - The ionic conductivity is about one order of magnitude higher than YSZ.
  - Electronic conductivity becomes significant for oxygen activity less than 10^{-14} atm.
- Characterized films of 16% Y:ZrO_2.
  - Ionic conductivity of <50 nm grain, one-micron thick films measured to room temperature (conductivity of the grains dominates).
  - Grain size <50 nm for annealing temperatures <800°C.
  - Produced >95% theoretical dense YSZ at 600°C.
- Characterized films of undoped and Gd doped CeO_2.
  - The electrical conductivity of both doped and undoped CeO_2 shows grain size dependence.
  - Ionic conductivity of nanocrystalline Gd doped CeO_2 less than that of the microcrystalline.
- Developed cathode substrate for deposition of 0.5- to 2-micron thick YSZ films for use as electrolyte in SOFCs.
  - Fabricated porous LSM substrates.
  - Synthesized nanoscale CeO_2 suspensions for deposition onto LSM substrate.
    - Control of cathode surface porosity to sizes <0.1 micron.
    - 3-5 micron thick CeO_2 layers planarize LSM substrate to surface roughness <0.1 micron.
- Produced electrolyte layers on porous cathode.
  - Transfer from dense substrate.
    - Rock salt substrate
    - Polyimide substrate
    - Transfer from polymer precursor.
- Developed composite YSZ films on both dense and porous substrates.
    - Fabricated 1-4μm thick dense YSZ films at <500 °C
    - Electrical conductivity of YSZ composite the same as dense sintered YSZ
- Completed Ph.D. studies of 2 students.

  Brian Gorman
    - Currently at North Texas University
    - He demonstrated important methods for preparing YSZ electrolytes on porous substrates.

  Zach Byars
    - Currently at Lilliputian Systems
    - He made significant progress on the understanding of impedance spectroscopy measurements on SOFC's.
- Developed 2 Patent Disclosures on processing of composite structures.

Approach

Fuel cell design by itself is a complicated problem. Many particular directions must be analyzed and solved to produce the final result, but there is no doubt that the combination of the materials involved in this design is a key issue. During the past few years there has been an effort promoted by the U.S. Department of Energy (SECA Program) to lower the operating temperature of solid oxide fuel cells. As a result, the solid oxide fuel cell activities at the Electronic Materials Applied Research Center (EMARC) of the University of Missouri-Rolla (UMR) have been focused on the fabrication of thin (0.5 to 5 μm thick), dense electrolyte layers of either zirconia or ceria. The route that has been taken is to deposit a polymer precursor solution, which contain the cations of the chosen electrolyte, onto a substrate and subsequently convert the resulting polymeric films into dense layers by thermal treatment.

The research that we have been doing over the last 7-8 years with support from both the Gas Research Institute and DOE has allowed us to develop the methods by which dense electrolyte layers of <5 microns in thickness can be attached to either the porous anode or porous cathode to yield an electrolyte/electrode structure which has the potential of being >100cm^2 in area. In addition, due to the nature of the process, it has the potential of being a very cost-effective method of building the electrolyte/electrode structures, which can operate in the 500 to 700°C range.

The process we are using involves the use of the patented (US Patent # 5,494,700) polymeric precursor technique, which was developed with GRI funding for the electrolyte layer deposition. Our experiments show that ceria films prepared from polymeric precursors have relatively high initial density (more than 85%) at temperatures as low as 400 °C and the density increases quickly with increasing temperature (we have practically dense film after annealing at 800 °C), shown in Figure 1. Grain size in these dense films is less than 100nm and we now can work with electrolyte thicknesses of <5μm.

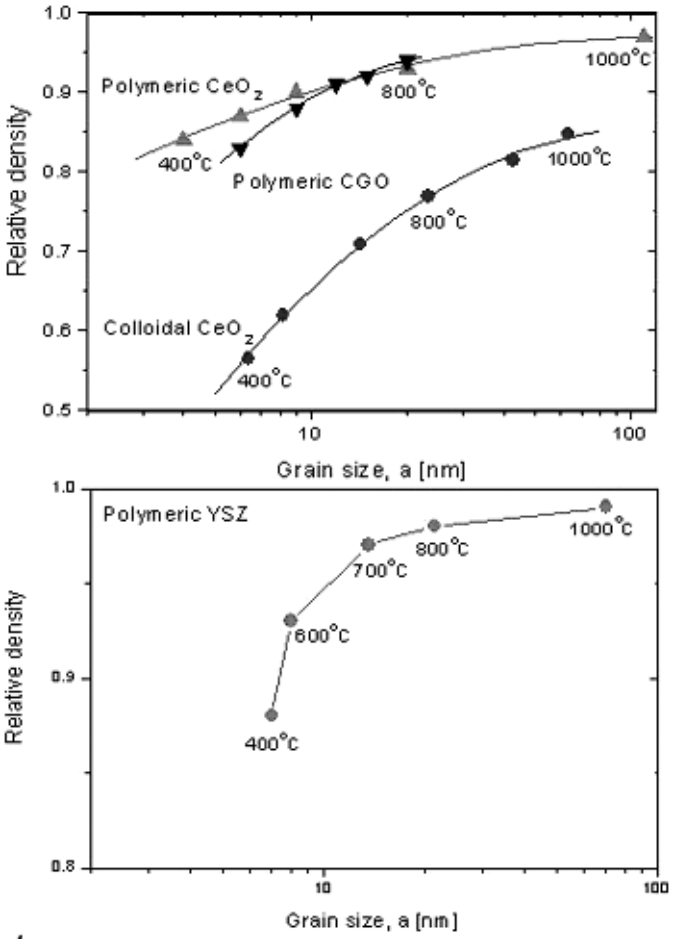

Figure 1. *Densification efficiency for polymeric films in comparison with colloidal suspensions*

The same situation takes place with YSZ polymeric films: it is possible to have dense film with good electrical properties at 800 °C, shown in Figure 2. Grain size is in the submicron region (less than 100nm) and electrolyte thickness. In addition, as shown in Figure 2, the polymer precursor method allows the densification temperature to be lowered by about 500 °C, compared to nanocrystalline powder.

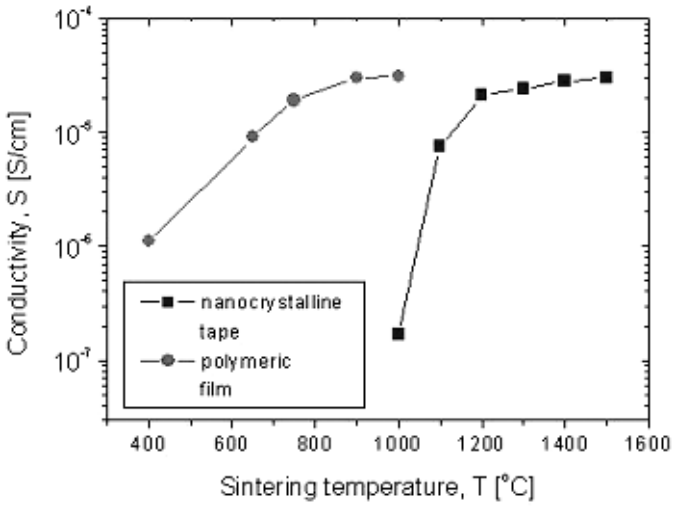

Figure 2. *Conductivity of YSZ tape and films as a function of annealing temperature.*

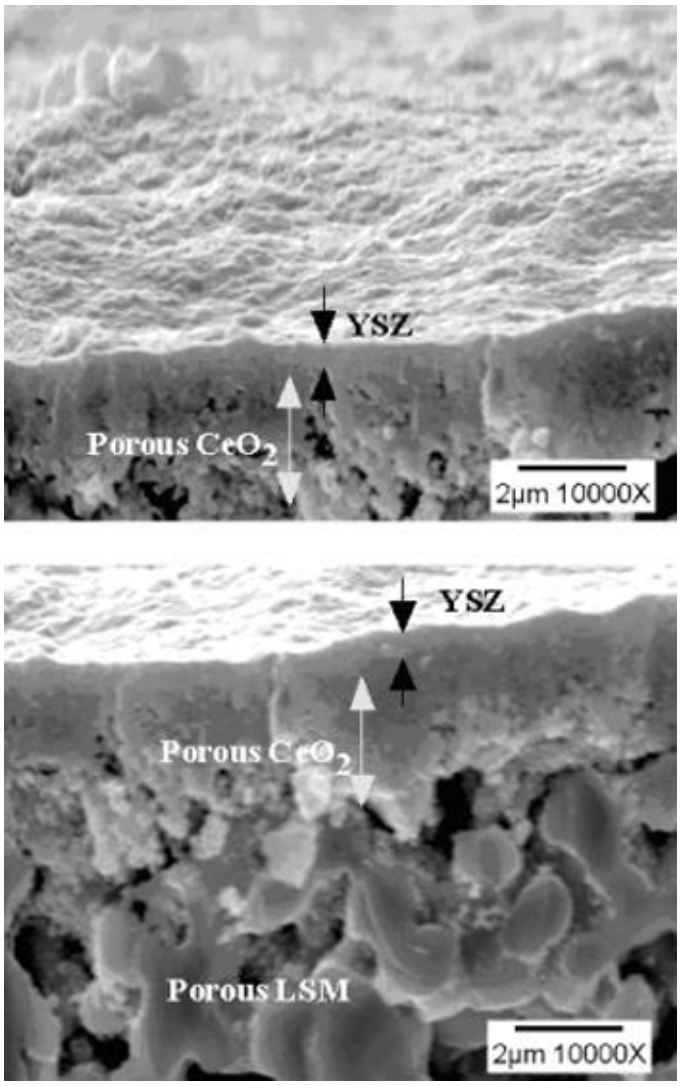

Figure 3. *SEM cross section images of YSZ/CeO2/LSM composite*

Results

We have shown in our previous investigations that nanocrystalline layers prepared from polymeric precursors are strong contenders for electrolyte preparation in SOFC design. It gives the possibility of preparation temperature about 800 °C while maintaining the grain size in the submicron level (see Figure 1 for SDC, and Figures 1 and 2 for YSZ). At the same time the density and the conductivity of the films are high. The problem with the polymeric precursors is the low cracking limit for one deposition, so we need to go with multiple depositions to build micron thick layers. In addition the polymer precursor process has difficulty in covering a surface which has pores >0.2microns in diameter. This presents a real limitation when we are trying to produce non-porous layers onto sintered porous electrodes. This has been a real "show stopper" for us for some time and has not been easy to solve. However, our studies on the current DOE contract have allowed us to arrive at a very good solution. The solution has two parts:

1. The development of a graded cathode structure that has pore diameters <1 micron on the surface.
2. The combination of polymeric precursors and nanocrystalline powder, which is shown in Figure 3.

A two-micron thick nanocrystalline CeO_2 layer was prepared from nanocrystalline CeO_2 powder and CeO_2 polymeric precursor at a temperature as low as 400 °C using only one deposition. This layer has ~50% porosity, but has strong bonding between the grains and substrate. The result of the impregnation of this layer by YSZ polymeric precursor is shown in Figure 3. It can be seen that we have a dense nanocrystalline layer about 1μm thick after this impregnation.

Conclusions & Future Activities

The combination of nanocrystalline powder and polymeric precursor extends the scope of the polymeric precursor application, and can open a new path to build cost-effective fuel cells with high performance that can be operated at temperatures in the 500-700 ^{o}C range.

This is the direction we are concentrating for the rest of this program, since it looks very practical and we have shown that non-porous composite electrolytes can be fabricated at temperatures below 900 ^{o}C for either YSZ or CGO electrolytes.

We are currently making structures of 2-5cm^2 in area, which consist of either dense YSZ or CGO infiltrated into a 2-5μm thick 50% porous layer made of either nanocrystalline CGO or YSZ powder. This composite structure coats a macroporous cathode or anode, which serves as the structural element of the bi-layer structure. An example of this structure is illustrated in Figure 3. These structures will be tested to determine their performance as SOFC elements.

References

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